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COMPLETE SPECIFICATION

Transparent Thermoplastic Composition of High Impact Resistance and manufacture thereof

We, TOYO RAYON KABUSHIKI KAISHA, a Japanese body corporate, of No. 2, 2-chome, Nihonbashi-Muromachi, Chuo-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention concerns thermoplastic compositions having special morphological characteristics wherein butadiene rubber particles in a specific particle size range are present in a thermoplastic matrix, and a method of manufacturing these compositions. The shaped articles obtained from these compositions, as compared with the conventional articles of this kind, possess a remarkably improved impact strength and seeing-through ability. (By the seeing-through ability is meant that an article has a good light transmission, is not coloured, and its surface does not cause diffused reflection, and that an object opposite the article can be seen through it. It cannot be judged just by the light transmission.)

Such polymers as polystyrene and polymethyl methacrylate have been relatively inexpensive and used widely as water-white transparent plastic materials. But the shaped articles obtained from such polymers are restricted in their use because of insufficient impact strength. It has been known that to remove this defect, an attempt was made to improve the impact strength of such an article by polymerising a monomer or monomeric mixture containing styrene in the presence of a rubbery material, and many proposals have been made with respect to the specific means of such a method. These improvements have culminated in such resins as represented by the so-called highly impact resistant poly-

styrene (may be referred to as HI polystyrene hereinafter) or ABS resin. These resins give excellent results as compared with the compositions which are obtained by polymerising the said monomer or monomeric mixture, and then blending the resulting polymer with a rubbery material.

Also bulk polymerisation, emulsion polymerisation and suspension polymerisation have been proposed to polymerise the same monomer or its mixture in the presence of a rubbery material.

It is inevitable that the rubber-modified polystyrene obtained by emulsion polymerisation is, although to varying degrees, coloured yellow to brown. On the other hand, it has been known that the rubber-modified polystyrene obtained by suspension polymerisation or bulk polymerisation is almost free of colouration. With respect to the rubber-modified polystyrene obtained by aqueous suspension polymerisation or bulk polymerisation, its impact strength is markedly lowered if the diameter of the rubbery material particles dispersed in the plastic material obtained is too small. For this reason, plastic materials in which the particles of the rubbery material with a particle diameter around $1-10\mu$ are dispersed have been actually used.

HI polystyrene can be cited as the conventional impact-resistant resin obtained by suspension polymerisation. A typical method of manufacturing such an impact-resistant resin is disclosed in British Patent No. 1,013,498 by which a solution of butadiene rubber in styrene is heat-polymerised in the absence of a catalyst, or pre-polymerised with an initiator (for instance, azo-bis-isobutyronitrile) having a relatively low grafting ability until phase-inversion occurs, and then the pre-polymer is

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subjected to suspension polymerisation by addition of an initiator having a large grafting ability (for instance, benzoyl peroxide).

Another proposal is disclosed in British Patent No. 1,009,360 according to which a polymerisation system composed of a rubbery substance and monomeric mixture whose refractive index (n_D^{25}) is within a specific range is subjected to bulk, suspension or emulsion polymerisation to give a rubber-modified HI polystyrene composition having a more improved transparency.

It is true that the impact strength of the shaped articles prepared from the materials obtained by these methods has been improved, but another disadvantage has become felt, namely that the material whose impact strength has been improved to a practical extent cannot be free from the sacrifice of the seeing-through ability which is the merit of polystyrene or poly(methyl methacrylate).

This seeing-through ability depends upon how vividly a distant view can be seen through an article shaped from a resinous material, and not merely upon the light transmission of the shaped article. For instance, even if plates A and B shaped under the same conditions respectively from two resin materials have substantially the same light transmission, it does not necessarily follow that they have the same seeing-through ability when a distant view is seen through each of these plates. On the contrary, it sometimes happens that when plate A has a better light transmission than plate B, plate B has a better seeing-through ability.

We have made extensive researches in an attempt to provide a colourless transparent, highly impact-resistant thermoplastic compositions having more improved high impact strength and also free from the lowering of seeing-through ability which shaped articles from rubber-modified HI polystyrene compositions having a more improved transparency have been unable to avoid, and a method of their manufacture. As a result, we have found that it is possible to manufacture highly impact-resistant thermoplastic compositions wherein butadiene rubber particles with a specific very small diameter are homogeneously dispersed in a thermoplastic matrix composed of a copolymer of a mono-alkenyl aromatic compound with an alkyl methacrylate, and that by these special compositions, both impact strength and seeing-through ability can be markedly improved concurrently, while an attempt in the prior proposals to satisfy one of these properties has inevitably resulted in worsening the other.

Furthermore, in spite of the fact that an attempt to improve the impact strength of a rubber-modified HI polystyrene cannot be free from the tendency of the decrease in yield strength, the highly impact-resistant

thermoplastic compositions of this invention having the said special morphological characteristics wherein butadiene rubber particles of a specific small size are homogeneously dispersed in the said matrix can substantially avoid the lowering of yield strength.

According to the present invention there is provided a highly impact-resistant transparent thermoplastic composition wherein butadiene rubber particles in an amount of 0.3 to 20% by weight occluding an isolated or substantially isolated copolymer, in an amount of 99.7 to 80%, by weight, of at least 70% by weight of a mono-alkenyl aromatic compound and an alkyl methacrylate are homogeneously dispersed in a continuous phase thermoplastic matrix composed of the said copolymer and wherein: (i) the average size of the said rubber particles is 0.15 to 0.7 μ and the butadiene rubber constituting the said particles occludes the said copolymer as spherical membranes having an average thickness of 0.0025 to 0.15 μ and not in excess of $\frac{1}{2}$ of the said average particle size; and, (ii) the difference in refractive index (n_D^{25}) between the said copolymer and the said butadiene rubber does not exceed 0.005. The preferred size of the rubber particles is 0.2 to 0.5 μ , the preferred thickness of the membranes is 0.005 to 0.1 μ , while the preferred range of proportions of the copolymer in the composition is 99 to 85%.

As the said butadiene rubber, polybutadiene or a butadiene-styrene copolymer having a styrene component in the amount up to 35% based on the weight of the copolymer is preferably used. The term "butadiene rubber" used in this invention is meant to include butadiene homopolymer and copolymers.

The preferred copolymers of a mono-alkenyl aromatic compound and an alkyl methacrylate are those in which at least 70% by weight of the comonomers are styrene and methylmethacrylate. At least one comonomer selected from methyl acrylate, ethyl acrylate, n-butyl acrylate and acrylonitrile can be cited as comonomers that may be included in the said copolymer in an amount of less than 30% by weight, preferably less than 20% by weight.

Styrene, α -methylstyrene and vinyl toluene are examples of the said mono-alkenyl aromatic compound, styrene being especially preferred. Suitable alkyl methacrylates are those of which the alkyl radical has 1-4 carbon atoms, methyl methacrylate being especially preferred.

The proportion of the mono-alkenyl aromatic compound to the alkyl methacrylate can be determined, as will be discussed later in this specification, depending upon the refractive index of butadiene rubber. In general, 15-60%, preferably 20-45%, by weight of

the mono-alkenyl aromatic compound is used against 85–40%, preferably 80–55%, by weight of the alkyl methacrylate.

According to this invention, it is essential that the said special morphological characteristics, the average particle diameter within the specific range, and the specific thickness of the spherical butadiene rubber membranes should be satisfied, and that the difference in refractive index (n_D^{25}) between the butadiene rubber and the copolymer of mono-alkenyl aromatic compound and alkyl methacrylate which constitutes the thermoplastic matrix and internal portion of the butadiene rubber particles should not be in excess of 0.005. The composition of the butadiene rubber and that of the monomeric mixture can be easily determined if the refractive index of the butadiene rubber and the polymer obtained by polymerising the monomeric mixture are measured in advance.

If a butadiene-styrene copolymer having a styrene content in excess of 35% by weight is used as the butadiene rubber, the glass transition temperature of the said copolymer gets high, and the impact strength at low temperature is not improved so much.

Furthermore, if in addition to styrene and methyl methacrylate, the said comonomers are used in an amount of not less than 30% by weight, the shaped articles obtained from the resulting compositions exhibit the deterioration in the seeing-through ability, heat distortion temperature, impact strength and yield strength which is mainly ascribable to the surface properties of the articles.

The most essential features of this invention will be explained with reference to the accompanying drawings.

A rubber-modified HI polystyrene composition wherein rubber particles are homogeneously dispersed in a continuous-phase thermoplastic matrix is known.

The present invention provides an impact-resistant thermoplastic composition with a remarkable combination of properties, namely a composition having the above first mentioned morphological characteristics under an optical microscope wherein the average size of the rubber particles is 0.15–0.7 μ and the said particles occlude the copolymer which is the same as one constituting the said matrix and which is isolated or substantially isolated therein. Usually, the said dispersion can be observed by an electronmicroscope with a magnification of 10,000 or so. A typical example of the electronmicroscopic view of the cross-section of the said structure is shown in Fig. 1, in which the black rings show butadiene rubber, and the other portion represents a copolymer of monoalkenyl aromatic compound and alkyl methacrylate. In Fig. 1 are seen black rings coalesced with each other. Hence, two or more rings coalesced with each

other are also within the scope of this invention, as long as they satisfy the particle size of the specific range. In this invention, the butadiene rubber particles dispersed in ones or twos shown in Fig. 1 account for about 50%, preferably 65%, of the total number of the rubber particles.

The special occluded structure expressed by this invention as "occluding a copolymer isolated or substantially isolated" is shown in Fig. 4 (i)–(iv), wherein (i) shows the structure which occupies most of the photo of Fig. 1, (ii) is an example of a plurality of rings coalesced with each other, (iii) shows a partly opened structure of the ring shown in (i), and (iv) is an assembly of two rings, a part of which is opened. It is conjectured that the shapes shown in (iii) and (iv) are also formed during the shaping of test samples to be observed under the electron-microscope in this invention.

By the expression "under an electronmicroscope" used in this invention is meant that observation is made by the electronmicroscopic photograph obtained by the following procedures.

A block of suitable size and shape for mounting on the specimen holder of an ultramicrotome is cut, and carefully trimmed at the tip to form a sharp pyramid. This specimen block should be cut from a shaped article at a position more than about 50 μ deep from the surface which is as flat as possible, and preferably at the centre of the shaped article. Moreover, the said position should not be the ends or weld line of the shaped article. It is mounted as usual on the specimen holder and cut preliminarily until the tip is truncated to a cutting area of about 0.5 mm square. The resin block is removed from the microtome and allowed to stand soaked in about 1% osmium tetroxide solution overnight. The dark-stained block is again mounted in the most elaborate manner this time in order to set up strictly on the previous position. The real cutting operation is started and it is tried to collect satisfactory sections within the range over which the fixing effect has reached.

Ultrathin section preparations obtained in this way are ready for electron microscopic examination. The rubber phase is shown as deeply stained particles dispersed in the less dense matrix of a styrenemethyl methacrylate copolymer. Representative results are shown in the accompanying figures.

The longest diameter of the butadiene rubber particle in the said photograph and the diameter crossing the longest diameter perpendicularly through its center are actually measured (unit being μ), which are referred to respectively as a and b , and the particle diameter r is calculated by the following equation.

$$\frac{a+b}{2}$$

The average particle diameter \bar{r} is determined by the following equation after measuring the diameters of 100 rubber particles chosen at random.

$$\bar{r} = \frac{\sum_{i=1}^m \eta_i r_i^4}{\sum_{i=1}^m \eta_i r_i^3}$$

(wherein η_i is the number of particles with a particle size of r_i ; and

$$\sum_{i=1}^m \eta_i = 100).$$

- 10 Sheets with a thickness of 3 mm prepared under the same shaping conditions respectively from a composition thermoplastic shown in Fig. 1 having the morphological characteristics and the average particle diameter specified in this invention and the already mentioned typical HI polystyrene (average particle diameter being 6μ) composition were compared with each other in respect of seeing-through ability. It was found that a distant view could be well seen through the former, while not only a distant view but also a near view could not be seen through the latter. The replica photographs of these sheets indicated that the former exhibited excellent smoothness, and the latter showed the surface like "frosted glass". The replica photograph of the first mentioned composition shown in Fig. 1 is attached as Fig. 2, and the replica photograph of the latter is shown as Fig. 3.
- 30 The replica photograph of a composition having the morphological characteristics of this invention but having an average particle diameter of 6μ , is the same as Fig. 3.

- 35 A remarkable difference in the surface state of the obtained shaped articles as representatively shown in Figs. 2 and 3 is also attributable to the difference of the highly impact-

resistant transparent thermoplastic compositions of this invention from the conventional compositions of this kind. In this invention, a combination of the morphological characteristic that the butadiene rubber particles occluding the said copolymer are homogeneously dispersed in the same copolymer matrix with the other conditions that the average size of the said particles is 0.15 to 0.7μ , the spherical membranes constituted by butadiene rubber have a thickness of 0.0025 to 0.15μ and less than $\frac{1}{2}$ of the said average particle diameter, and that the difference between the refractive index of the copolymer and that of the said butadiene rubber is less than 0.005 is of importance. The reason is that the above-mentioned morphological characteristic serve to give shaped articles provided with excellent seeing-through ability, a high impact strength and yield strength which have been unable to coexist together, in spite of the fact that the particle size below 1μ has hitherto been avoided in the technological field to which this invention pertains to improve the impact strength to a sufficiently satisfactory degree.

The following Table 1 shows the physical properties of the shaped article prepared under the same conditions from a typical product which satisfies the morphological characteristics and the particle diameter as specified in this invention, a product having the previously known shape and particle size and a product having the morphological characteristics of this invention but not satisfying the particle diameter, thickness of the membranes and the difference in refractive index as specified in this invention. The values of the physical properties are expressed by the arithmetic mean of the results of six tests. The shapes and the particle diameters were measured as already mentioned, and the physical properties were measured according to the procedures mentioned later before the Examples. The shaped articles consisted of 5% of polybutadiene and 95% of a styrene-methylmethacrylate copolymer of 29.5% of styrene and 70.5% of methylmethacrylate. The difference in refractive index between the rubber component and the said copolymer is 0.003.

TABLE 1

Morphological properties shown in Fig. 1	Rubber particle size ()	Thickness of rubber membrane ()	Isod Impact strength (kg/cm ² of notch)	Yield Strength (kg/cm ²)	Haze value (%)	Colouring of shaped article	Light transmission (visible rays : %)
Present invention	Yes	0.3	0.01	8.1	550	5	No
Comparison p	Yes	0.1	0.01	2.1	620	5	No
Comparison q	No (structure similar to that of H1 polystyrene)	5.0	—	3.7	430	65	No
Comparison r	No (butadiene rubber particle consists substantially of said rubber) *1	0.35	—	5.2	540	20	Yes (yellow)
Comparison s	No (amorphous) *2	—	—	5.3	250	60	No
Control	No (only the matrix component) —	—	—	1.7	680	4	No
							93

(Note:) *1 Prepared by emulsion polymerisation.

*2 Suspension polymerisation from the outset.

The haze value, light transmission and colouring are the standard of judging the seeing-through ability.

5 As shown in Table 1, there is a remarkable difference in the improvement of the properties which are difficult to obtain together and in the prevention of the degradation of desirable properties among the conventional articles (comparisons r and s), articles having the morphological characteristics specified in this invention but without the average particle size defined in this invention (comparisons p and q), and the article of this invention, with the matrix component alone used as a control.

To produce highly impact-resistant thermoplastic compositions having the morphological characteristics, particle size, membrane thickness and difference in refractive index as defined in this invention, the reaction is carried out in the presence of a polymerisation initiator, chosen from the hitherto

known radical polymerisation catalysts which is soluble in the monomers which compose the matrix, and is difficultly soluble in water. The presence of such an initiator is advantageous in realising the morphological characteristics, the particle size membrane thickness, and difference in refractive index defined in this invention.

It is not known why such initiators as above mentioned are very suitable particularly in obtaining the products equipped with the said four requirements, and others are not. But, for example, even if such initiators as acetyl peroxide, caprylyl peroxide, methyl ethyl ketone peroxide, hydroxyheptyl peroxide, 2 - azo - isobutyronitrile, lauroyl peroxide, and cyclohexanone peroxide are used, it is difficult or virtually impossible to realise the above-mentioned four requirements. Specific examples of the initiators suitable for use in this invention will be described later.

According to the process of this invention, a butadiene rubber solution in a monomeric mixture is first subjected to bulk polymerisation. Whether this solution is a true solution does not matter, and the solution looks an ordinary solution, clearly different from a suspension or emulsion; the solution acts however like an emulsion in that it is susceptible to phase inversion.

The steps of the process of making the composition of this invention (in which process of course the starting materials must be selected so as to be capable of giving the desired dispersion of rubbery particles) are as follows: (a) mixing 0.3 to 20 parts by weight of a substantially non-cross-linked butadiene rubber with 99.7 to 80 parts by weight of a monomeric mixture of which at least 70% by weight consists of a mono-alkenyl aromatic compound and an alkyl methacrylate to form a butadiene rubber solution in the said monomeric mixture, (b) subjecting the resulting solution to bulk polymerisation in the presence of a polymerisation initiator, which is soluble in said comonomers and difficultly water-soluble, while stirring to cause phase inversion of the solution and form droplets comprising copolymer derived from the monomeric mixture within an occluding membrane of butadiene rubber, the droplets being dispersed within a matrix derived from the monomeric mixture, said polymerisation being effected until 5—35% by weight of said monomeric mixture is copolymerised, (c) when necessary, mixing the resulting prepolymer dispersion with a solution of the butadiene rubber in the monomeric mixture or with a prepolymer derived therefrom, in such proportions as to introduce droplets of greater or smaller average particle size as may be required, and (d) subjecting the resulting prepolymer system to an aqueous suspension polymerisation, or (d') subjecting the said pre-

polymer system to bulk polymerisation without substantial stirring.

The polymerisation of step (b) is carried out while stirring. This stirring should neither be too vigorous nor too slow, and the actual stirring conditions ought to be determined experimentally. If the stirring operation is omitted in this bulk polymerisation, a product provided with the said four requirements cannot be obtained. The polymerisation temperature is not particularly restricted, and usually a temperature of 40 to 150°C. is used.

The said bulk polymerisation is conducted until 5 to 35% by weight of the said monomeric mixture is polymerised. Either when the polymerisation proceeds beyond that extent or when it does not reach that extent, a final product is, more or less, prevented from having the said four requirements.

Thus, the polymerisation is continued until at least the phase inversion is substantially completed, and a pre-polymer system containing droplets of the rubber solution occluding the copolymer of the said monomeric mixture can be obtained.

It is essential that the starting polymerisation system to form the said pre-polymer system should be a butadiene rubber solution in a monomeric mixture consisting of 0.3 to 20, preferably 1 to 15, parts by weight of a substantially non-crosslinked butadiene rubber and 99.7 to 80, preferably 99 to 85, parts by weight of the said monomeric mixture of which at least 70% is composed of a mono-alkenyl aromatic compound and an alkyl methacrylate. It is necessary to increase the light transmission of the said compositions to these monomers in the monomeric mixture within the above-mentioned range so that the difference in refractive index (n_D^{25}) between the butadiene rubber and the copolymer of the said monomeric mixture in the final product may not be in excess of 0.005.

An appropriate amount of the initiator is 0.01 to 2.0 parts by weight based on 100 parts by weight of the entire starting polymerisation system. Many other conditions can be varied so long as it is possible to obtain a final product equipped with the above-mentioned four requirements. The expression "substantially non-crosslinked" is a term which also means such a crosslinkage that the entire starting polymerisation system can be apparently an ordinary solution in the sense already mentioned. Usually, a butadiene rubber with a gel content of not more than 5% by weight is used.

As the said butadiene rubber, a substantially non-crosslinked polybutadiene or a butadiene-styrene copolymer having a styrene component in an amount not in excess of 35% based on the weight of the copolymer

is advantageously used. Preferable monomeric mixtures to form the matrix are a mixture of styrene with methyl methacrylate and a mixture at least 70% by weight of styrene and methyl methacrylate and less than 30% by weight of other known comonomer copolymerisable therewith. As such known comonomers, methyl acrylate, ethyl acrylate, n-butyl acrylate and acrylonitrile are preferably used.

As the very suitable polymerisation initiators, we can cite benzoyl peroxide, tert-butyl perbenzoate, dicumyl peroxide, di-isopropyl benzene hydroperoxide, 2,5 - dimethyl - 2,5-bis(benzoylperoxy)hexyne, tert-butyl perisobutyrate, di - tert. - butyl di - perphthalate, di-tert. - butyl di-perterephthalate, 2,5 - dimethyl - 2,5 - bis(tert. - butylperoxy)hexyne, tert-butyl peracetate, tert-butyl-cumyl peroxide, cumene hydroperoxide, di-tert-butyl peroxide, p-chlorobenzoyl peroxide and 2,4-dichlorobenzoyl peroxide.

From the commercial standpoint and also the ease of controlling of operations to give a final product the said four requirements, preferable examples of the initiator are benzoyl peroxide, dicumyl peroxide, di-isopropylbenzene hydroperoxide, 2,5 - dimethyl-2,5 - bis(benzoylperoxy)hexyne, tert-butyl perisobutyrate, di - tert. - butyl - diperphthalate, di - tert. - butyl - di - perterephthalate, 2,5-dimethyl - 2,5 - bis(tert. - butyl - peroxy)-hexyne, and tert-butylcumyl peroxide.

The use of the butadiene rubber in an amount in excess of the proportion of the butadiene rubber and the monomeric mixture as specified above not only makes it difficult to carry out the second stage of polymerisation to a final product subsequent to the pre-polymerisation, but also constitutes a bar against the provision of the said four requirements required of the final product.

Incidentally, the polymerisation may be carried out in the presence of a known chain-transfer agent such as mercaptanes, e.g., n-dodecylmercaptane and a dimer of α -methyl styrene.

In order, therefore, to form the pre-polymer system of this invention, the following steps are essential. Namely,

- (a) mixing 0.3 to 20 parts by weight of a substantially non-crosslinked butadiene rubber with 99.7 to 80 parts by weight of a monomeric mixture of which at least 70% consists of a monoalkenyl aromatic compound and an alkyl methacrylate to form a butadiene rubber solution in the said monomeric mixture, and
- (b) subjecting the resulting solution to bulk polymerisation with stirring in the presence of a polymerisation initiator which is soluble in the said comonomers and difficultly water-soluble until 5 to 35% by weight of the said comonomers are polymerised.

In accordance with this invention, a second-stage polymerisation is carried out subsequent to the said first-stage polymerisation in order to obtain a final product. This second-stage polymerisation should preferably be an aqueous suspension polymerisation, but can also be a bulk polymerisation without a substantial stirring. Such polymerisation can be performed after adding to the pre-polymer system formed by step (b) containing droplets of the rubber solution occluding the copolymer of the said monomeric mixture, a pre-polymer system prepared separately or a material system (a) mentioned above including a system polymerised to an optional extent before reaching the pre-polymer stage (in this invention, these are inclusively expressed as a butadiene rubber solution in a monomeric mixture or a partially polymerised butadiene rubber solution. This addition, step (c), is advantageous for adjusting the size of the said droplets to such an extent as to satisfy the particle size of a final product, when the said droplets in the pre-polymer system obtained by the first-stage polymerisation are either too large or too small to satisfy the particle size and the membrane thickness required of the final product. (In fact, the droplets are swelled, and the size thereof cannot be directly measured. The suitability of the droplets can be easily judged if a test piece is subjected to the second-stage polymerisation.)

If the second-stage polymerisation gives the droplets with an average particle size in excess of 0.7μ , there is added as step (c) a pre-polymer system which will form small particles by the same polymerisation. On the other hand, when the second-stage polymerisation gives the droplets having an average particle size of less than 0.15μ , there is added as step (c) a material system (a) or its partially polymerised butadiene rubber solution which will form large particles by the same polymerisation in order to effect the above-mentioned adjustment. If the pre-polymer system consists of droplets which, when polymerised, come to have a particle size in excess of 0.7μ , it is especially desirable to add thereto a prepolymer system which is obtained by the first-stage polymerisation carried out until 5 to 35% by weight of the comonomers are polymerised and which will give an average particle size of 0.05 to 0.5μ by the second-stage polymerisation in an amount of 60 to 90% based on the total weight of the resulting mixture. When the obtained droplets as a pre-polymer system will give an average particle size of less than 0.15μ , it is especially desirable to add thereto a pre-polymer system which is obtained by the first-stage polymerisation carried out until 25% by weight of the monomers are polymerised (i.e., containing the material system (a) as such) and which will give an

average particle size of 0.5 to 10 μ or a network shape (the network shape is representative of a case where the said monomers are polymerised in an amount of not over 25% by weight and phase inversion does not occur) in an amount of 10 to 40% based on the total amount of the resulting mixture.

When an aqueous suspension polymerisation method according to (d) is employed, it is a matter of course to carry out the second-stage polymerisation after forming an aqueous suspension system by adding a suspending agent and water to the pre-polymer system.

The polymerisation initiator may or may not be added to this system. But in this second-stage polymerisation, a radical catalyst unsuitable for a first-stage polymerisation can be used. The same initiator as used in the first-stage polymerisation is preferable. The

amount of the initiator to be added is the same as in the case of the first-stage polymerisation. The polymerisation temperature is usually 40 to 150°C, similar to the case of the first-stage polymerisation. As the suspend-

ing agent used in the suspension polymerisation, a known inorganic suspending agent such as barium sulphate or calcium phosphate and a known organic suspending agent such as polyvinyl alcohol and polyacrylic acid salt can be cited, and any suspending agent usable generally in the suspension polymerisation can be used.

The polymerisation may be carried out with the use of a chain-transfer agent similarly to the first-stage polymerisation. When step (c) is followed by step (d), it is possible to carry out the second-stage polymerisation after a pre-polymer system obtained in the first-stage polymerisation has been mixed with a butadiene rubber solution in the monomeric mixture or the said solution in partially polymer-

ised form and the mixture is subjected to the second-stage polymerisation to form an aqueous suspension system. In this case, 5 to 35% of the monomers in the mixture should be polymerised similarly to the case of the first-stage polymerisation. When bulk polymerisation of the said (b) and (c) is employed, it is necessary to carry out the bulk polymerisation without substantial stirring so that the shapes of the droplets of the rubber solution occluding the copolymer of a monomeric mixture formed in the pre-polymer system may not be destroyed.

With respect to the particulars of the polymerisation initiator, the same can be said as in the case of suspension polymerisation. The reaction temperature and the use of a chain-transfer agent are the same as those mentioned with respect to the suspension polymerisation.

When step (c) is followed by step (d), the procedure is similar to (c) and (d) as above except that bulk polymerisation is carried out.

The so obtained highly impact-resistant transparent thermoplastic composition of this invention can be used *in situ* as a shaping composition. But a known phenolic anti-oxidant such as 2,6-di-tert-butyl-4-methyl phenol, a known organic phosphite, a known plasticizer, lubricant or an anti-static agent can be incorporated into the said composition to make a shaping composition. The amount of the anti-oxidant, plasticizer, lubricant and anti-static agent used is suitably not in excess of 5%, preferably 2%, of the weight of the said composition.

The measurement of the physical properties of a highly impact-resistant transparent thermoplastic composition of this invention is done by the following procedures.

Conditioning and Testing: 23°C., 55% RH

Izod impact strength (notched) (kg cm/cm of notch):

ASTM D 256—56

Yield strength (kg/cm²):

ASTM D 638—58 (pulling speed: 2 cm/min.)

Haze value (%) and light transmission (%) (at visible rays):

ASTM D 1003—52 with respect to a plate having a thickness of 3 mm.

(A test piece was obtained by injection moulding at 220°C.)

In the Examples which follow, only the haze value is shown as the measure for judging the seeing-through ability of the shaped articles. The reason is that as in any shaped article in which the difference in refractive index (n_D^{25}) between the said copolymer and

the said butadiene rubber does not exceed 0.005, its light transmission is within the range of 83 to 90%, the seeing-through ability can be judged only by the haze value.

The haze values in the following Tables show the following seeing-through ability.

Haze value: The value of a sheet with a thickness of 3 mm, as measured according to ASTM D 1003—52.

- © Haze value 4 — 10%
(a distant view can be very well seen through a piece of moulded article)
- Haze value 10 — 30%
(a distant view can be well seen through a piece of moulded article)
- Δ Haze value 30 — 50%
(a distant view cannot be well seen through a piece of moulded article)
- × Haze value more than 50%
(a distant view cannot be seen through a piece of moulded article)
- × × Haze value more than 50%
(even a near view cannot be seen through a piece of moulded article, the difference in refractive index between the said copolymer and the said butadiene rubber is more than 0.005)

These symbols will be used hereinafter.

In the following Examples a polymerisable solution consisting of substantially non-cross-linked butadiene rubber and vinyl monomers prepared by the following procedures was used.

Five parts by weight of substantially non-crosslinked polybutadiene ($\eta_{sp}^{25} = 1.516$) was dissolved into a monomeric mixture composed

of 28 parts by weight of styrene and 67 parts by weight of methyl methacrylate (the refractive index at 23°C. (n_D^{25}) of a copolymer obtained by polymerization of the said mixture being 1.513) to form a polymerisable solution (A).

In the same manner, various polymerizable solutions shown in Table 2 were prepared.

TABLE 2

Polymer- izable solution	Monomers (part by weight)						Rubber (parts by weight)			Difference between η_{sp}^{100}/c , res and η_{sp}^{100}/c , rub	
	Styrene	Methyl methacrylate	Methyl acrylate	Ethyl acrylate	n-Butyl acrylate	Acrylonitrile	Refractive index of the resin component η_{sp}^{100}/c , res	Polybutadiene	Butadiene-styrene copolymer		Refractive index of rubber component η_{sp}^{100}/c , rub
A	28	67	—	—	—	—	1.513	5	—	1.516	0.003
B	39	54	—	—	—	—	1.532	—	7 (styrene content) 25%	1.534	0.002
C	32.5	56.5	10	—	—	—	1.517	1	—	1.516	0.001
D	32.7	56.8	10	—	—	—	1.517	0.5	—	1.516	0.001
E	28	70	—	—	—	—	1.512	2	—	1.516	0.004
F	99	—	—	—	—	—	1.595	1	—	1.516	0.079
G	95	—	—	—	—	—	1.595	5	—	1.516	0.079
H	33	54	—	10	—	—	1.521	3	—	1.516	0.005
I	30	53	—	10	—	—	1.519	7	—	1.516	0.003
J	39	56	—	—	—	—	1.531	—	5 (styrene content) 24%	1.535	0.004
K	31	54	10	—	—	—	1.514	5	—	1.516	0.002
L	42	53	—	—	—	—	1.536	—	5 (styrene content) 24%	1.535	0.001
M	27	63	—	—	—	5	1.521	5	—	1.516	0.005
N	29	61	—	—	5	—	1.512	5	—	1.516	0.004
O	38	57	—	—	—	—	1.531	—	5 (styrene content) 24%	1.535	0.004
P	27	68	—	—	—	—	1.512	5	—	1.516	0.004

EXAMPLE 1

(1) Five hundred grams of the solution (A) was put into a ground type flask equipped with a nitrogen inlet tube, a condenser, a thermometer and an agitator, followed by the addition of 2.5 g of benzoyl peroxide as a radical polymerization initiator. After dissolving these in each other at room temperature until the solution was apparently homogeneous, the rotation of the agitator was adjusted to 400 rpm. Polymerization was carried out for 4 hours and 20 minutes at a temperature of 70°C., and when the conversion rate reached 20%, the product was cooled with ice to room temperature thereby to form a prepolymer (1). As a matter of course, phase inversion occurred in this prepolymer. To the pre-polymer (1) was added 0.5 g of n-dodecylmercaptane, and the mixture was agitated until it became homogeneous. On the other hand, a ground type flask equipped with a nitrogen inlet tube, a thermometer and an agitator was charged with one litre of water, 5 g of sodium salt of polyacrylic acid and 2 g of sodium hydrogencarbonate to make a solution of these. The pre-polymer (1) was added to this solution, and the mixture was subjected to suspension polymerization at 70°C. with the agitator operated at 500 rpm. This suspension polymerization was carried out for 3 hours at 70°C., 2 hours at 80°C., and finally 2 hours at 90°C. until its completion, the temperature being raised stepwise. The resulting polymeric composition was filtered, washed with water, dried, and then pelletised.

The pelletised product was injection moulded at 220°C. The surface of the so obtained moulded article was very smooth,

and a distant view could be seen well through it.

(2) To 1.0 kg of the solution (A) was added 2.0 g of benzoyl peroxide. The mixture was polymerized in the same manner and a prepolymer with a conversion ratio of 18% was obtained. The prepolymer was admixed with 2.0 g of benzoyl peroxide and 1.0 g of di-tert-butyl peroxide, and the mixture was subjected to suspension polymerization in the same manner. The resulting polymeric composition was pelletised, and injection moulded at 220°C. The surface of the moulded article was very smooth, and a distant view could be seen well through it. The electronmicroscopic view (30,000 magnification) of the internal structure of the polymeric composition obtained above is shown in Fig. 1, and the replica photograph thereof is shown in Fig. 2 (200 magnification).

(3) Various polymerizable solutions shown in Table 3 were polymerized with the use of various polymerization initiators in the same manner to give various polymeric compositions. The properties of the moulded articles obtained from these compositions are shown in Table 3.

With reference to Table 3, when a composition wherein the average particle size of the rubber is greater than 0.7μ , e.g., a polymeric composition obtained by the use of lauroyl peroxide as an initiator in the prepolymerization, was injection moulded at 220°C., the obtained moulded article had a rough surface, and it was impossible to see a distant view through it. The surface replica photograph of this article was not so different from that shown in Fig. 3.

TABLE 3.

Polymer- soluble solution	Pre-polymerization Conditions		Properties of Shaped Articles (23°C.)			
	Initiator	Conversion ratio (%)	Izod impact strength (kg. cm/cm of notch)	Average size of the dispersed particles of rubber (μ)	Thickness of rubber membrane (μ)	Average size of the resin particles in rubber membrane
A	benzoyl peroxide	20	7.2	0.22	0.01	0.19
A	"	18	8.1	0.3	0.01	0.28
A	azo-bis-isobutyronitrile	20	2.1	5.4	—	—
A	lauroyl peroxide	19	2.7	6.4	—	—
A	tert-butyl peroctanate	20	4.2	at least 1 (amorphous)	—	—
A	cyclohexanone peroxide	13	3.2	5	—	—
A	p-menthane hydroperoxide	18	3.2	8	—	—
A	methyl-ethyl ketone peroxide	16	8.9	5 — 10	—	—
A	2,5-dimethyl-2,5-bis(tert- butylperoxy)hexane	15	8.0	2	—	—
B	benzoyl peroxide	24	7.4	0.3	0.01	0.28
M	"	16	7.4	0.25	0.01	0.22
N	"	16	7.1	0.25	0.01	0.23

Comparative
Example

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EXAMPLE 2

- (1) Benzoyl peroxide (5.0 g) was dissolved in 1.0 kg of the polymerizable solution (A), and the solution was polymerized in the same manner as in Example 1 until the conversion ratio reached 11% to give a pre-polymer (2—1). 500 g of this pre-polymer was subjected to suspension polymerization in the same manner as in Example 1 to form a polymeric composition.
- (2) Benzoyl peroxide (5.0 g) was dissolved in 1.0 kg of the said solution (A), and the resulting solution was polymerized in the same manner until the conversion ratio reached 31% to give a pre-polymer (2—2). 500 g of this pre-polymer was subjected to suspension polymerization to form a polymeric composition.
- (3) Benzoyl peroxide (5.0 g) was dissolved in 1.0 kg of the said solution (A) in the same manner until the conversion ratio reached 30% to give a pre-polymer (2—3). 500 g of this pre-polymer was likewise subjected to suspension polymerization to form a polymeric composition.
- (4) A solution of 2.5 g of benzoyl peroxide in 500 g of the said solution (A) was, without pre-polymerization, subjected to suspension polymerization to obtain a polymeric composition.
- (5) 400 g of the pre-polymer (2—1) was mixed with 100 g of the pre-polymer (2—2), and 100 g of the pre-polymer (2—1) was mixed with 400 g of the pre-polymer (2—2). These two mixtures were respectively subjected to suspension polymerization to give two polymeric compositions.
- (6) 400 g of the pre-polymer (2—3), 100 g of the solution (A) and 0.5 g of benzoyl peroxide were mixed with one another, and the mixture was subjected to suspension polymerization to give a polymeric composition.
- The properties of the moulded products obtained from the compositions according to the above (1) to (6) are shown in Table 4.

TABLE 4

Comparative Example	Experiment number	Composition of pre-polymer (%)	Properties of Shaped Articles (23°C.)					As resin having excellent transparency and impact strength
			Izod impact strength (23°C)(notched) (kg. cm/cm of notch)	Average size of the dispersed particles of rubber (μ)	Thickness of rubber membrane (μ)	Average size of the resin particles in rubber membrane (μ)	Haze	
1	(2-1)	100	8.1	amorphous	—	—	×	unsuitable
2	(2-2)	"	2.3	0.11	—	—	⊙	"
3	(2-3)	"	2.6	0.11	—	—	⊙	"
4	solution (A)	"	5.3	amorphous	—	—	×	"
5	{ (2-1) (2-2) (2-1) (2-2) (2-3)	{ 80 20 20 80 80	{ 7.9 7.6 7.9 7.6 7.9	{ 0.80 0.25 0.80 0.25 0.30	{ — 0.01 — 0.01 0.02	{ — 0.20 — 0.20 0.20	{ Δ ⊙ — ⊙ ○	{ unsuitable " " " suitable "
6	solution	20	7.9	0.30	0.02	0.20	○	"

EXAMPLE 3

This Example concerns the polymeric compositions having very little rubber content, properties of the moulded articles are shown in Table 5.

ization method as mentioned in Example 1.

The pre-polymerization conditions and the

properties of the moulded articles are shown

in Table 5.

TABLE 5

Solution	Pre-polymerization conditions		Properties of Shaped Articles (23°C.)				
	Initiator	Conversion ratio (%)	Izod impact strength (notched) (kg.cm/cm of notch)	Average size of dispersed particles of rubber (μ)	Thickness of rubber membrane (μ)	Average size of the resin particles in rubber membrane (μ)	Haze
(C)	benzoyl-peroxide	21	3.5	0.25	0.01	0.23	⊙
(C)	"	37	2.0	0.10	—	—	⊙
(C)	azo-bis-isobutyronitrile	24	2.1	6.0	—	—	×
(D)	benzoyl-peroxide	18	3.0	0.35	0.01	0.33	○
(E)	"	20	5.0	0.25	0.01	0.22	⊙
(F)	"	22	1.6	0.35	—	—	××

Comparative
Example
Comparative
Example

Comparative
Example

F (especially when styrene alone is used as the monomeric component), there can only be obtained a resin poor in transparency and impact strength.

EXAMPLES 4—19

Various polymerizable solutions (500 g) were respectively pre-polymerized in the same manner as in Example 1 with the use of the various initiators suitable for use in this invention. Benzoyl peroxide (1.5 g) was dissolved apparently homogeneously in each of the obtained prepolymeres. The solutions obtained were respectively subjected to suspension polymerization in the same manner as in Example 1. The properties of the moulded articles obtained from the resulting polymeric compositions are shown in Table 6.

As is clear from Table 5, when the initiators suitable for use in this invention are used, the moulded articles obtained from the polymeric compositions of this invention have an excellent impact strength and transparency, even if the rubber content is less than 2%. Even in this case, however, resins with excellent impact strength cannot be obtained if the average size of the dispersed rubber particles is below 0.15 μ . Furthermore, if such an initiator as azo-bis-butyronitrile which is not suitable for use in this invention is employed, there is only obtained a resin which is poor in transparency and impact strength. If, on the other hand, the difference in refractive index between the rubber component and the resin component is greater than 0.005 as in the case of solution

TABLE 6

Ex-ample No.	Solution (g)	Pre-polymerization conditions				Properties of Shaped Articles (23°C)				
		Initiator	Amount of initiator used (mol)	Temperature (°C)	Time (hr)	Izod impact strength (21°C) (kg cm/cm notched)	Average size of the dispersed particles of rubber (μ)	Thickness of rubber membrane (μ)	Average size of the film in rubber membrane (μ)	Haze
4	(A) 500g	Di-cumyl peroxide	5×10^{-3}	98	3.5	6.3	0.35	0.02	0.25	○
5	(A) 500g	Tert-butylperacetate	4.13×10^{-3}	85	5.3	6.8	0.3	0.03	0.15	○
6	(A) 500g	Tert-butyl perisobutyrate	"	75	5.5	5.8	0.35	0.03	0.15	○
7	(A) 500g	Tert-butyl perbenzoate	"	85	4.6	6.7	0.35	0.02	0.15	○
8	(A) 500g	2,5-dimethyl-2,5-bis(tert-butyl peroxy)hexyne	"	95	3.3	8.3	0.3	0.03	0.1	○
9	(A) 500g	2,5-dimethyl-2,5-bis-(benzoylperoxy)hexyne	"	98	7	7.3	0.4	0.03	0.15	○
10	(A) 500g	Di-tert-butyl dipenthatate	"	95	4	9.5	0.4	0.03	0.1	○
11	(A) 500g	Di-tert-butyl diperterephthalate	"	90	6	9.1	0.4	0.03	0.1	○
12	(A) 500g	p-chloro-benzoylperoxide	"	70	1.5	6.4	0.25	0.01	0.23	⊙
13	(A) 500g	2,4-dichloro-benzoylperoxide	"	70	1.5	5.6	0.25	0.02	0.2	⊙
14	(A) 500g	Tert-butyl cumyl peroxide	"	95	5.5	7.2	0.32	0.01	0.3	⊙
15	(A) 500g	Cumene hydroperoxide	"	90	3.3	7.7	0.3	0.02	0.2	⊙
16	(A) 500g	Di-tert-butylperoxide	"	98	5	8.2	0.35	0.03	0.2	○
17	(K) 500g	Benzoylperoxide and 2,5-dimethyl-2,5-bis(benzoylperoxy)hexyne respectively	2.07×10^{-3} each initiator	90	2	9.4	0.3	0.02	0.25	⊙
18	(K) 500g	Di-isopropylbenzene hydroperoxide	3.9×10^{-3}	98	5	7.3	0.3	0.02	0.15	○
19	(L) 500g	Di-cumylperoxide	5.56×10^{-3}	98	5	5.7	0.3	0.02	0.25	⊙

- EXAMPLE 20
1 Kg of the solution (A) was put into a 2-litre flask equipped with a nitrogen inlet tube, a condenser, a thermometer and an agitator, followed by the addition of 1 g of benzoyl peroxide. The mixture was made into an apparently homogeneous solution. The flask was then immersed in a vessel at 70°C., and the solution was polymerized for 4.5 hours with the agitator operated at 400 rpm. A pre-polymer with a conversion ratio of 15.4% was obtained. After cooling, 400 g of the pre-polymer was put into a one-litre flask. One gram of n-dodecylmercaptane was added thereto. Each of 100 g of the obtained solution was put into a glass ampule and immersed in a constant temperature bath. The solution was polymerized for 10 hours at 100°C., 5 hours at 130°C., 5 hours at 150°C., 5 hours at 200°C., and finally one hour at 210°C., and polymeric compositions were obtained.
- EXAMPLES 21—41
500 g of each polymerizable solution was pre-polymerized with the use of 4.13×10^{-4} mole of each of the initiators in the same manner as described in Example 20. The obtained pre-polymer was polymerized in the same manner as in Example 20, the latter half of the polymerization being a bulk polymerization substantially without agitation. Table 7 shows the properties of the moulded articles obtained from the polymeric compositions of Examples 20—41.

TABLE 7

Example No.	Solution	Pre-polymerization conditions		Properties of Shaped Articles (23°C)			
		Initiator	Conversion ratio (%)	Izod impact strength (kg. cm/cm notched)	Average size of the dispersed particles of rubber (μ)	Thickness of rubber membrane (μ)	Average size of the resin particles in rubber membrane (μ)
20	(A)	Benzoyl peroxide	15.4	6.6	0.3	0.02	0.25
21	(I)	Benzoyl peroxide	14.6	5.6	0.4	0.03	0.15
22	(A)	Dicumyl peroxide	15.2	6.2	0.3	0.02	0.25
23	(A)	Tert-butyl perbenzoate	14.5	5.9	0.5	0.02	0.3
24	(A)	Di-isopropylbenzene hydroperoxide	15.3	5.9	0.4	0.03	0.2
25	(A)	2,5-dimethyl-2,5-bis(benzoyl peroxy)hexane	15.1	6.6	0.3	0.02	0.2
							Haze
							◎
							○
							◎
							○
							○
							○

TABLE 7 (Continued)

Example No.	Solution	Pre-polymerization conditions		Properties of Shaped Articles (23°C)				Haze
		Initiator	Conversion ratio (%)	Izod impact strength (kg. cm/cm notched)	Average size of the dispersed particles of rubber (μ)	Thickness of rubber membrane (μ)	Average size of the resin particles in rubber membrane (μ)	
26	(A)	Tert-butyl perisobutyrate	14.0	5.4	0.3	0.03	0.15	○
27	(A)	Di-tert-butyl-dipercphthalate	15.4	6.3	0.25	0.03	0.15	○
28	(A)	Di-tert-butyl dipercetephthalate	15.2	6.5	0.3	0.03	0.15	○
29	(A)	2,5-dimethyl-2,5-bis(tert-butyl-peroxy)hexyne	15.8	6.2	0.3	0.03	0.2	○
30	(A)	Tert-butylcumyl peroxide	15.3	6.9	0.5	0.03	0.2	○
31	(A)	2,4-di-chloro-benzoyl peroxide	15.2	7.0	0.4	0.02	0.15	○
32	(A)	p-chloro-benzoyl peroxide	15.8	5.8	0.3	0.01	0.27	⊙
33	(A)	Azo-bis-isobutyronitrile	15.2	2.6	4.5	—	—	×
34	(A)	Benzoyl peroxide	37.2	2.1	0.1	—	—	⊙
35	(A)	Lauroyl peroxide	15.8	2.4	3.6	—	—	×
36	(A)	Cyclohexanone peroxide	13.4	3.2	6.8	—	—	×
37	(A)	Hydroxyheptyl peroxide	15.0	5.4	5.2	—	—	×
38	(A)	Hydroxycyclohexyl peroxide	15.3	2.2	6.3	—	—	×
39	(A)	Tert-butyl peracetate	14.4	6.0	0.5	0.03	0.2	○
40	(A)	Cumene hydroperoxide	15.2	6.6	0.35	0.02	0.2	○
41	(A)	Di-tert-butyl peroxide	15.3	7.2	0.35	0.03	0.15	○

Comparative
Example

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Comparative

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EXAMPLE 42 polymerizable solutions with the use of various radical initiators in an amount of 5
 The pre-polymers as shown in Table 8 were prepared by partially polymerizing the 8.26×10^{-3} mole per kilogram.

TABLE 8

Solution	Pre-polymerization conditions		Pre-polymer
	Initiator	Conversion ratio (%)	
(A)	dicumyl peroxide	12.5	[44—1]
(A)	dicumyl peroxide	30	[44—2]
(A)	tert-butylperbenzoate	29	[44—5]
(A)	di-isopropylbenzene hydroperoxide	28	[44—6]
(A)	2,5-dimethyl-2,5 bis(benzoyl-peroxy)hexyne	28	[44—7]
(A)	tert-butyl perisobutyrate	30	[44—8]
(A)	di-tert-butyl di-perphthalate	26	[44—9]
(A)	di-tert-butyl di-perterephthalate	27	[44—10]
(A)	2,5-dimethyl-2,5 bis(tert-butyl-peroxy) hexyne	27	[44—11]
(A)	tert-butylperacetate	28	[44—12]
(A)	lauroyl peroxide	29	[44—13]
(A)	azo-bis-isobutyronitrile	30	[44—14]
(A)	p-menthane hydroperoxide	30	[44—15]
(A)	cyclohexanone peroxide	30	[44—16]
(A)	benzoyl peroxide	11.4	[44—17]
(O)	tert-butylperacetate	28	[44—18]

Benzoyl peroxide (1.5 g) was dissolved in 500 g of each of the so obtained pre-polymers, and each solution was subjected to suspension polymerization. The properties of the moulded articles obtained from the resulting polymeric compositions are shown in Table 9.

TABLE 9

Pre-polymer	Izod impact strength (23 °C) (kg cm/cm notched)	Average size of the dispersed particles of rubber	Haze	As resin having excellent transparency and impact strength	
solution (A)	5.3	amorphous	×	unsuitable	
solution (O)	4.8	amorphous	×	"	
[44-1]	7.8	0.85	Δ	"	For comparison
[44-2]	2.7	0.1	⊙	"	
[44-5]	2.5	0.1	⊙	"	
[44-6]	3.3	0.05 — 0.1	⊙	"	
[44-7]	5.3	0.25	○	suitable	
[44-8]	2.3	0.1	⊙	unsuitable	For comparison
[44-9]	6.6	0.2	⊙	suitable	
[44-10]	7.1	0.2	⊙	"	
[44-11]	5.1	0.3	○	"	
[44-12]	6.5	0.2	⊙	"	
[44-13]	2.8	at least 3	×	unsuitable	For comparison
[44-14]	2.6	" 2	×	"	
[44-15]	2.4	" 3	×	"	
[44-16]	1.9	" 3	×	"	
[44-17]	9.9	amorphous	×	"	
[44-18]	5.6	0.3	○	suitable	

In the meantime, mixtures of these pre-polymers in various combinations were prepared, and a solution of 1.5 g of benzoyl peroxide in 500 g of each of these mixtures was subjected to suspension polymerization. The properties of the moulded articles obtained from the resulting polymeric compositions are shown in Table 10 below.

TABLE 10

Ex. No.	Pre-polymer composition (%)	Izod impact strength (23°C.) (kg cm/cm notched)	Average size of the dispersed particles of rubber (μ)	Thickness of rubber film (μ)	Average size of the resin particles rubber film (μ)	Haze	For comparison	
							As resin having excellent transparency and impact strength	For Comparison
1	[44-1] : [44-2] 80 : 20 " " 20 : 80	7.2 7.0	0.75 0.25	0.02	0.15	Δ	unsuitable	For comparison
2	[44-2] : [solution (A)] 80 : 20 " " 20 : 80	7.7 8.1	0.35 0.83	0.03	0.15	○	suitable	For Comparison
3	[44-5] : [44-17] 80 : 20	8.0	0.25	0.02	0.15	⊙	unsuitable	
4	[44-6] : [44-17] 80 : 20 [44-6] : [44-17] 70 : 30	6.9 8.0	0.2 0.2	0.02 0.02	0.1 0.15	⊙	suitable	
5	[44-7] : [44-17] 80 : 20	8.8	0.4	0.03	0.1	○	suitable	
6	[44-8] : [44-17] 80 : 20	7.2	0.25	0.03	0.15	⊙	suitable	
7	[44-9] : [44-17] 80 : 20	9.6	0.35	0.03	0.1	○	suitable	
8	[44-10] : [44-17] 80 : 20	9.7	0.35	0.03	0.1	○	suitable	
9	[44-11] : [44-17] 90 : 10 [44-11] : [44-17] 80 : 20	7.8 8.4	0.45 0.45	0.03 0.03	0.1 0.1	○	suitable	
10	[44-12] : [44-17] 80 : 20	8.9	0.3	0.03	0.15	⊙	suitable	
11	[44-13] : [44-17] 80 : 20	7.5	above 3	—	—	×	unsuitable	For comparison
12	[44-14] : [44-17] 80 : 20	6.3	"	—	—	×	unsuitable	
13	[44-15] : [44-17] 80 : 20	8.2	"	—	—	×	unsuitable	
14	[44-16] : [44-17] 70 : 30	8.1	"	—	—	×	unsuitable	
15	[44-18] : [solution (O)] 80 : 20	7.1	0.3	0.02	0.25	⊙	suitable	

EXAMPLE 43

The pre-polymers as shown in Table 11 were prepared by partially polymerizing the said solutions with the use of various radical initiators in an amount of 8.26×10^{-3} mole per kilogram.

TABLE 11

Solution	Pre-polymerization conditions		Pre-polymer
	Initiator	Conversion ratio (%)	
(P)	Benzoyl peroxide	15.4	[45— 1]
(P)	Dicumyl peroxide	29.4	[45— 4]
(P)	Tert-butyl perbenzoate	30.2	[45— 5]
(P)	Di-isopropylbenzene hydroperoxide	28.3	[45— 6]
(P)	2,5-dimethyl-2,5-bis(benzoyl peroxy)hexyne	29.4	[45— 7]
(P)	Tert-butyl perisobutyrate	29.1	[45— 8]
(P)	Di-tert-butyl diperphthalate	29.5	[45— 9]
(P)	Di-tert-butyl diperterephthalate	28.6	[45—10]
(P)	2,5-dimethyl-2,5-bis(tert-butyl-peroxy)hexyne	30.2	[45—11]
(P)	Tert-butyl peracetate	27.6	[45—12]
(P)	Tert-butylcumyl peroxide	29.5	[45—13]
(P)	2,4-dichloro-benzoyl peroxide	28.7	[45—14]
(P)	p-chloro-benzoyl peroxide	28.0	[45—15]
(P)	Lauroyl peroxide	30.4	[45—16]
(P)	Cyclohexanone peroxide	28.6	[45—17]
(P)	Hydroxy heptyl peroxide	29.0	[45—18]
(P)	Hydroxy cyclohexyl peroxide	29.4	[45—19]
(P)	Cumene hydroperoxide	29.2	[45—20]
(P)	Di-tert-butyl peroxide	27.0	[45—21]
(P)	Benzoyl peroxide	11.2	[45—22]

Each of these pre-polymers was singly subjected to bulk polymerization. The properties of the moulded articles obtained from the resulting polymeric compositions are shown in Table 12.

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TABLE 12

Pre-polymer	Izod impact strength (23°C.) (kg. cm/cm notched)	Average size of the dispersed particles of rubber (μ)	Haze	As resin having excellent transparency and impact strength	
solution (P)	6.3	amorphous	×	unsuitable	For comparison
45-1	6.6	0.3	⊙	suitable	
45-4	2.5	0.1	⊙	unsuitable	For comparison
45-5	2.3	0.1	⊙	unsuitable	
45-6	2.4	0.1	⊙	unsuitable	
45-7	5.2	0.25	○	suitable	
45-8	2.1	0.1	⊙	unsuitable	For comparison
45-9	5.4	0.2	○	suitable	
45-10	5.6	0.2	⊙	suitable	
45-11	5.1	0.3	○	suitable	
45-12	5.8	0.2	⊙	suitable	For comparison
45-13	2.5	0.1	⊙	unsuitable	
45-14	2.7	0.1	⊙	unsuitable	
45-15	2.3	0.05-0.1	⊙	unsuitable	
45-16	2.4	3.5	×	unsuitable	
45-17	2.4	5.5	×	unsuitable	
45-18	2.1	5.5	×	unsuitable	
45-19	2.6	5.0	×	unsuitable	
45-20	2.6	0.1	⊙	unsuitable	
45-21	2.2	0.1	⊙	unsuitable	
45-22	7.7	amorphous	×	unsuitable	

In the meantime, mixtures of these pre-polymers in various combinations were prepared, and various polymeric compositions were obtained by subjecting them to bulk polymerization. The properties of the moulded articles obtained from the resulting compositions are shown in Table 13.

TABLE 13

Experiment No.	Pre-polymer composition (%)	Izod impact strength (23°C.) (kg cm/cm notched)	Average size of the dispersed particles of rubber (μ)	Thickness of rubber membrane (μ)	Average size of the resin particles in rubber membrane (μ)	Haze	As resin having excellent transparency and impact strength
1	[45-1]: [solution (P)] 80:20	7.5	0.35	0.02	0.15	◎	suitable
2	[45-1]: [solution (P)] 20:80	7.5	1.7	—	—	×	unsuitable
3	[45-4]: [45-22] 80:20	6.2	0.3	0.02	0.2	○	suitable
4	[45-5]: [45-22] 80:20	5.6	0.2	0.02	0.15	◎	23
5	[45-5]: [45-22] 80:20	5.8	0.2	0.03	0.1	◎	23
6	[45-7]: [45-22] 80:20	7.1	0.30	0.02	0.2	○	23
7	[45-8]: [45-22] 80:20	6.4	0.25	0.02	0.2	◎	23
8	[45-9]: [45-22] 80:20	7.3	0.25	0.03	0.15	○	23
9	[45-10]: [45-22] 80:20	7.4	0.25	0.03	0.15	◎	23
10	[45-11]: [45-22] 80:20	7.1	0.4	0.03	0.2	○	23
11	[45-12]: [45-22] 80:20	7.3	0.3	0.02	0.25	○	23
12	[45-13]: [45-22] 80:20	6.3	0.3	0.03	0.2	○	23
13	[45-14]: [45-22] 80:20	5.4	0.25	0.03	0.15	◎	23
	[45-15]: [45-22] 80:20	5.9	0.25	0.02	0.2	◎	23

For comparison

TABLE 13 (Continued)

Experiment No.	Pre-polymer composition (%)	Impact strength (23°C.) (kg cm/cm notched)	Average size of the dispersed particles of rubber (μ)	Thickness of rubber membrane (μ)	Average size of the resin particles in rubber membrane (μ)	Haze	As resin having excellent transparency and impact strength	For Comparison
14	[45-16] : [45-22]	5.3	3.1	—	—	×	unsuitable	
15	[45-17] : [45-22]	5.4	4.7	—	—	×	30	
16	[45-18] : [45-22]	4.4	4.8	—	—	×	30	
17	[45-19] : [45-22]	6.2	4.3	—	—	×	30	
18	[45-20] : [45-22]	8.1	0.2	0.03	0.1	◎	suitable	
19	[45-21] : [45-22]	7.6	0.25	0.03	0.17	◎	30	

WHAT WE CLAIM IS:—

1. A highly impact-resistant, transparent thermoplastic composition wherein butadiene rubber particles in an amount of 0.3 to 20% by weight, excluding an isolated or substantially isolated copolymer, in an amount of 99.7 to 80% by weight, of at least 70% by weight of a mono-alkenyl aromatic compound and an alkyl methacrylate are homogeneously dispersed in a continuous phase thermoplastic matrix composed of the said copolymer and wherein:

- (i) the average size of the said rubber particles is 0.15 to 0.7 μ and the butadiene rubber constituting the said particles occludes the said copolymer as spherical membranes having an average thickness of 0.0025 to 0.15 μ , and not in excess of $\frac{1}{4}$ of the said average particle size; and,

- (ii) the difference in refractive index (n_D^{25}) between the said copolymer and the said butadiene rubber does not exceed 0.005.

2. A composition according to claim 1 wherein the said copolymer is derived from 15 to 60% by weight of a mono-alkenyl aromatic compound and 85 to 40% by weight of an alkyl methacrylate.

3. A composition according to claim 1 or 2 wherein the monoalkenyl aromatic compound is styrene, α -methyl styrene or vinyl toluene.

4. A composition according to claim 1, 2 or 3 wherein the alkyl group of the alkyl methacrylate has 1 to 4 carbon atoms.

5. A composition according to claim 4 wherein the alkyl methacrylate is methyl methacrylate.

6. A composition according to claims 3

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and 5 wherein at least 70% by weight of the comonomers from which the said copolymer is derived comprises styrene and methyl methacrylate.

- 5 7. A composition according to claim 6 wherein the said copolymer contains, in addition to styrene and methyl methacrylate, less than 30% by weight of at least one comonomer selected from methyl acrylate, ethyl acrylate, n-butyl acrylate and acrylonitrile.

- 10 8. A composition according to any preceding claim, wherein the said butadiene rubber is polybutadiene or a butadiene-styrene copolymer containing a styrene component in an amount not in excess of 35% based on the weight of the copolymer.

- 15 9. An impact-resistant thermoplastic composition according to claim 1 substantially as hereinbefore described.

- 20 10. A method for the manufacture of an impact-resistant transparent thermoplastic composition as claimed in claim 1 which comprises the steps of:

- (a) mixing 0.3 to 20 parts by weight of a substantially non-cross-linked butadiene rubber with 99.7 to 80 parts by weight of a monomeric mixture of which at least 70% consists of a monoalkenyl aromatic compound and an alkyl methacrylate to form a butadiene rubber solution in the said monomeric mixture,

- (b) subjecting the resulting solution to bulk polymerisation in the presence of a polymerisation initiator, which is soluble in said comonomers and difficultly water-soluble, while stirring to cause phase inversion of the solution and form droplets comprising copolymer derived from the monomeric mixture within an occluding membrane of

butadiene rubber, the droplets being dispersed within a matrix derived from the monomeric mixture, said polymerisation being effected until 3-35% by weight of said monomeric mixture is copolymerised,

- (c) when necessary, mixing the resulting prepolymer dispersion with a solution of the butadiene rubber in the monomeric mixture or with a prepolymer derived therefrom, in such proportions as to introduce droplets of greater or smaller average particle size as may be required, and

- (d) subjecting the resulting prepolymer system to an aqueous suspension polymerisation, or

- (d') subjecting the said prepolymer system to bulk polymerisation without substantial stirring.

11. A method according to claim 10, wherein the said polymerisation initiator is selected from benzoyl peroxide, tert-butyl perbenzoate, dicumyl peroxide, di-isopropyl benzene hydroperoxide, 2,5 - dimethyl - 2,5-bis(benzoylperoxy)hexyne, tert-butyl perisobutyrate, di-tert-butyl di-perphthalate, di-tert-butyl di-perterephthalate, 2,5 - dimethyl - 2,5 - bis(tert-butylperoxy)hexyne, tert-butyl peracetate, ter-butyl - cumyl peroxide, cumene hydroperoxide, di-tert-butyl peroxide, p-chlorobenzoyl peroxide and 2,4-dichlorobenzoyl peroxide.

12. A method of making an impact-resistant thermoplastic composition according to claim 10 and substantially as hereinbefore described.

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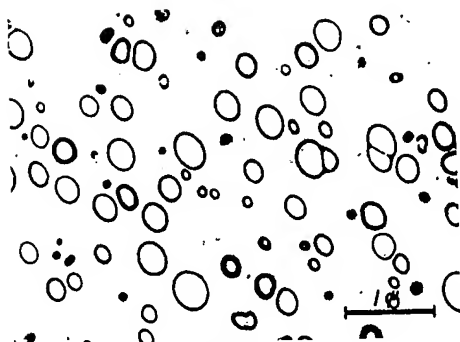


Fig. 1.

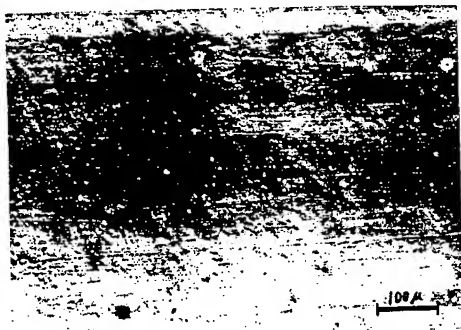


Fig. 2.

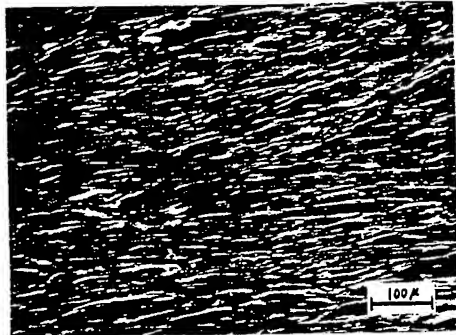


Fig. 3

Fig. 4

(i)



(ii)



(iii)



(iv)

